

Determination of Adsorbed CO Molecular Orbital Positions by Photoelectron Diffraction

Xin Zhou^{1,2}, Guorong Zhuang¹, Yufeng Chen¹, Scot A. Kellar³, Edward J. Moler¹, Zahid Hussain¹,
and David A. Shirley¹

¹Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, CA 94720

²Department of Physics, The Pennsylvania State University, University Park, PA 16802

³Department of Applied Physics, Stanford University, Stanford, CA 94305

The molecular orbitals of intact molecules adsorbed on metal surfaces display spectra akin to those of the free molecule, but typically with shifts in properties such as relative binding energies and vibrational frequencies. The stability of such systems is usually attributed to electron redistribution between the substrate and the molecular orbitals of the adsorbate: this redistribution characterizes the surface chemical bond. For example, in the Blyholder model [1] of CO adsorbed on a transition metal surface atom, in the linear geometry M-C-O, the CO 5σ orbital is polarized toward the transition-metal atom M, accompanied by the “back donation” of this atom's d-orbital electron density into the unoccupied CO $2\pi^*$ orbital, while the CO 4σ orbital remains concentrated in the C-O bond. This model accounts for the observed spectral properties, but more direct experimental evidence for the spatial distribution of the CO orbitals would be valuable. We present such evidence below.

Adsorbate structural studies by photoelectron diffraction have involved measuring the positions of substrate scattering atoms relative to the effective centroid of a photoelectron “source” orbital, an atomic core orbital in an adsorbate atom or molecule. The centroid of such a core orbital is located, of course, at the atomic nucleus: hence analysis of the photoelectron diffraction data establishes the position of this nucleus, and with it the atomic structure of the adsorbate-surface system.

The present work was performed on the system $c(4\times 2)2\text{CO}/\text{Pt}(111)$. Three source orbitals were used, in three separate measurements: the C 1s core orbital, as described above, to establish the position of the carbon atom, which is used as a fiducial reference point, and two molecular orbital peaks, which also show large-amplitude photoelectron diffraction oscillations. These oscillations reflect the effective centroids of the 4σ and 5σ orbitals, respectively, along the Pt-C-O axis, with the 4σ centroid falling between C and O, and the 5σ centroid between Pt and C.

While photoelectron diffraction is commonly associated with core electrons, this effect was apparently first observed with valence electrons, both in the scanned-angle mode [2] and in the scanned-energy mode [3], where it was observed in the present system and interpreted as photoelectron diffraction. Diffraction has been reported in photoelectrons from both localized and itinerant valence bands, in nickel [4] and aluminum [5], respectively. However, the present work is the first to interpret molecular-orbital based photoelectron diffraction to determine the location of adsorbate molecular orbitals.

The experiment was performed in an ultra-high vacuum chamber equipped for angle-resolved photoemission on beamline 9.3.2 at the Advanced Light Source in Lawrence Berkeley National Laboratory. The platinum crystal was repeatedly cleaned during the experiment by sputtering and annealing cycles. Surface cleanliness and order were periodically checked with synchrotron XPS and LEED. The CO gas was introduced into the chamber through a leak valve. The desired $c(4\times 2)$ LEED pattern was consistently reproduced by backfilling the chamber at room

temperature with CO at 1×10^{-6} torr for 10 seconds, as described in the literature [6]. The sample surface temperature was kept at 110K throughout the data collection. The photon polarization vector was oriented 30° from the sample surface normal direction, along which photoelectrons were collected.

The energy-dependent intensity of the C 1s core-level peak, and those of the CO 4σ and $(5\sigma + 1\pi)$ peaks, were measured as functions of the photoelectron momentum wave vector, $I(k)$. To facilitate Fourier-transform analysis, data were collected at small and equal k intervals over wide energy ranges in each case. The molecular-orbital data confirmed the earlier [3] measurements, which were relatively sparse and over a smaller photon energy range. After careful peak-fitting and data reduction by standard procedures, a $\chi(k)$ curve,

$$\chi(k) = \frac{I(k) - I_0(k)}{I_0(k)}$$

was generated for each (peak) data set. These are depicted in Fig. 1.

Large intensity oscillations in $I(k)$ were observed with normal-emission photoelectrons from

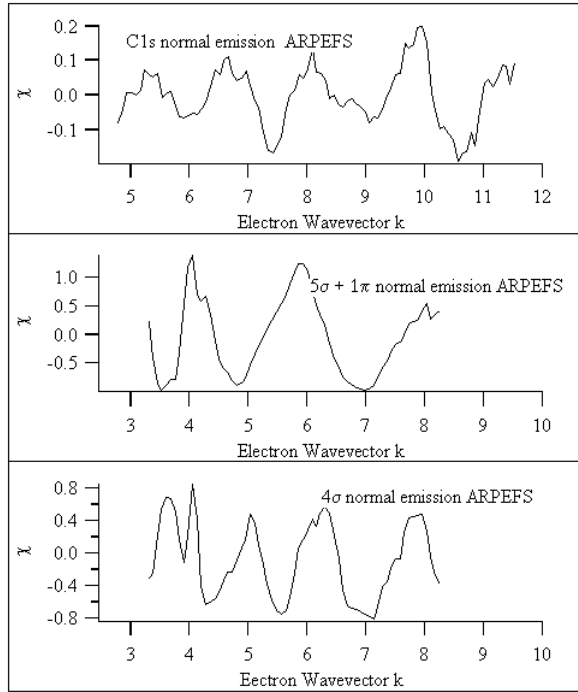


Fig. 1. The three χ curves. The unit of the horizontal axis is \AA^{-1} .

all three peaks. Visual inspection of the three $\chi(k)$ curves reveals a single strongest frequency in each case, albeit with different values from one curve to the next. *This appears to indicate that the effective centroids of the photoelectron initial-state orbitals lie at different points along the Pt-C-O axis.*

The C 1s data confirm the local adsorbate site geometry of the accepted $c(4 \times 2)$ surface structure. To date, the only published results on the distances between the carbon atoms and the platinum surface at those two different adsorption sites were obtained in a low energy electron diffraction (LEED) experiment by Ogletree, Van Hove and Somorjai [11], which gave C-Pt interplanar distances of 1.85\AA and 1.55\AA at the top and bridge site respectively.

In this analysis, we modeled the angle-resolved photoemission extended fine structure (ARPEFS) [12] $\chi(k)$ curve with a cluster-model multiple-scattering code using the Rehr-Albers separable propagator [13]. The Pt lattice constant

was fixed at 3.923\AA . The C-O bond length was fixed at 1.130\AA , as it should not be affected much by the platinum surface. The C 1s photoelectron scattering effects are quite insensitive to the position of the oxygen atoms in this geometry and in the fixed-angle-scanned-energy mode [14]. As noted above, all symmetry-allowed adsorption sites were considered in the simulation and indeed the accepted model gives the smallest R-factor. Upon minimization of the R-factor, the C-Pt interplanar distances were found to be $1.452 \pm 0.002 \text{\AA}$ at the bridge site and $1.828 \pm 0.001 \text{\AA}$ at the top site (statistical errors only!), corresponding to a Pt-C bond length of 2.008\AA , in excellent agreement with the LEED result of Ogletree, Van Hove and Somorjai. systematic errors, common to all electron-scattering methods, limit the ultimate accuracy at this time to no better than $\pm 0.01 - 0.02 \text{\AA}$.

Before turning to a discussion of the molecular orbitals, we note that the C 1s Fourier transform spectrum is dominated by a single peak at 4Å. This arises from the atop site, in which the C-O axis is collinear with the strongly-backscattering Pt atom in the configuration Pt-C-O. A similar dominance is also expected to hold for the 4σ and 5σ molecular orbitals, and the 1π orbital is expected to contribute little signal along the normal direction. We shall therefore interpret the molecular orbital spectra below in terms of the position of the 4σ and 5σ orbitals along the atop-site Pt-C-O axis.

Having determined the positions of the atop-site C atoms in the c(4×2)2CO/Pt(111) system, we can now use them as fiducial markers for the molecular orbitals, in the approximation that most of their normal photoemission intensity variations arise from backscattering off the Pt atoms in the atop sites. We interpret these data by the same methods used for structural studies by ARPEFS with core levels. By thus determining the effective mean positions of the molecular orbital electron distributions along the Pt-C-O axis relative to the Pt scatterer, we can test the putative polarization of the 5σ orbital toward the surface, as required to form the surface chemical bond accordingly to the Blyholder model.

The wavefunctions for an atop adsorbate system were depicted, e.g., by Rhodin and Gadzuk [15]. However, we do not have quantitative adsorbate wave functions to compare with.

As noted above, our normal emission data in the form of an intensity ratio compare favorably with similar, but much more limited, measurements done much earlier [3]. Both of the molecular orbital χ curves oscillate by nearly 100%, much more than the C1s core-level χ curve. The Fourier transform of the 4σ χ curve shows one dominant peak at 4.8Å, a larger path-length difference (PLD) than the main peak of C1s FT at 4.0Å, while the 5σ+1π FT shows one dominant peak at 3.3Å, a smaller PLD than C1s FT. This confirms our inferences from visual inspection of the three χ curves in Fig. 1. We therefore infer that the centroids of the three orbitals along the Pt-C-O axis fall in the order 4σ > C1s > 5σ relative to the Pt atom, with the 4σ in the C-O bond and the 5σ centroid between Pt and C, as predicted in the Blyholder model.

To model the molecular-orbital photoelectron diffraction in this system in an approximate way, we used a linear combination of atomic orbitals (LCAO) model to simulate the CO molecular orbitals and a Pt 5dz² orbital on the Pt atom for the top sites only. This atomic approach should provide a qualitatively correct, albeit an oversimplified, model. We calculated separately the final state wavefunctions of diffracted photoelectrons from Pt 6s, Pt 6p, Pt 5d, C 2s, C 2p, O 2s and O 2p atomic orbitals, and linearly combined these wavefunctions to simulate the observed final state that would originate from the molecular orbitals.

As the LCAO/MO coefficients are not known, especially for this adsorbate system, we elected to use the same data reduction process as for core-level photoemission to produce χ_E and χ_T , and varied the atomic orbital coefficients to minimize the R-factor. This kind of coefficient determination is independent of any conventional theoretical calculation of the LCAO coefficients based on cluster models: thus it could in principle provide a test of such *ab initio* models. The prospect of using photoelectron diffraction from molecular orbitals to study chemical bonds in this way poses a challenge for theoretical advances in seriously modeling the surface chemical bond, as well as photoemission from that bond. As we have no *ab initio* results to compare with, at this time we can only assess whether the coefficients from our minimization procedure appear to be reasonable. Apparently they do: 4σ = 1.000 C2s + 5.763 C2p - 5.521 O2p; 5σ = 7.365 C2s + 3.380 C2p + 4.720 Pt6s + 3.500 Pt6p + 1.510 Pt 5d. The Fourier transforms of the χ curves show credible, if mediocre, fits. In particular, the very large amplitude modulations in χ are modeled, as are the single dominant low-PLD peaks.

We have observed and interpreted photoelectron diffraction from molecular orbitals. The C-Pt interplanar distances of $c(4\times 2)2\text{CO}/\text{Pt}(111)$ are determined as 1.83Å at the top site and 1.45Å (2.01Å Pt-C bond length) at the bridge site, with systematic uncertainties of ca. 0.01-0.02Å. The 4σ orbital has an effective electron-density centroid between the C and O atoms, while for the 5σ orbital this centroid lies between the C and the Pt atoms. This experiment demonstrates the capability of photoelectron diffraction for studying the surface chemical bond.

We thank Dr. J.J. Rehr of University of Washington for generously providing the platinum phase shifts calculated with the FEFF 7.0 code, Dr. P.H.T. Philipsen of Vrije Universiteit, The Netherlands, for LCAO calculation of a free CO molecule, Dr. A. McLean of Queen's University, Canada, for providing a fast algorithm for calculating Voigt function.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Principal investigator: David A. Shirley, Ernest Orlando Lawrence Berkeley National Laboratory.
Email: dshirley@lbl.gov.

REFERENCES

1. G. Blyholder, J. Chem. Phys. **68**, 2772 (1964).
2. K. Siegbahn, U. Gelius, H. Siegbahn, and E. Olson, Phys. Lett. **32A**, 221 (1970); Physica Scripta, **1**, 272 (1970).
3. D.A. Shirley, J. Stöhr, P.S. Wehner, R.S. Williams, and G. Apai, Physica Scripta **16**, 398 (1977).
4. S.D. Kevan, D.H. Rosenblatt, D.R. Denley, B.-C. Lu, D.A. Shirley, Phys. Rev. B **20**, 4133 (1979).
5. J. Osterwalder, T. Greber, S. Hüfner, and L. Schlapbach, Phys. Rev. Lett. **64**, 2683 (1990).
6. H. Steininger, S. Lehwald, and H. Ibach, Surf. Sci. **123**, 264 (1982); I.J. Malik and M. Trenary, *ibid.* **214**, L237 (1989).
7. J. Wintterlin, S. Völkening, T.V.W. Janssens, T. Zambelli, and G. Ertl, Science **278**, 1931 (1997), and references therein.
8. H. Froitzheim, H. Hopster, H. Ibach, and S. Lehwald, Appl. Phys. **13**, 147 (1977).
9. G. Apai, P.S. Wehner, R.S. Williams, J. Stöhr, and D.A. Shirley, Phys. Rev. Lett. **37**, 1497 (1976).
10. J.W. Davenport, Phys. Rev. Lett. **36**, 945 (1976).
11. D.F. Ogletree, M.A. Van Hove, and G.A. Somorjai, Surf. Sci. **173**, 351 (1986).
12. J.J. Barton, C.C. Bahr, Z. Hussain, S.W. Robey, J.G. Tobin, L.E. Klebanoff, and D.A. Shirley, Phys. Rev. Lett. **51**, 272 (1983).
13. J.J. Rehr and R.C. Albers, Phys. Rev. B **41**, 8139 (1990).
14. J.J. Barton, S.W. Robey, and D.A. Shirley, Phys. Rev. B **34**, 778 (1986).
15. T.N. Rhodin and J.W. Gadzuk, in *The Nature of the Surface Chemical Bond*, edited by T.N. Rhodin and G. Ertl (North-Holland, Amsterdam, 1979), Chap. 3.